Quantum stochastic resonance in parity violating chiral molecules

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In order to explore parity violating effects in chiral molecules, of interest in some models of evolution towards homochirality, quantum stochastic resonance (QSR) is studied for the population difference between the two enantiomers of a chiral molecule (hence for the optical activity of the sample), under low viscous friction and in the deep quantum regime. The molecule is described by a two-state model in an asymmetric double well potential where the asymmetry is given by the known predicted parity violating energy difference (PVED) between enantiomers. In the linear response to an external driving field that lowers and rises alternatively each one of the minima of the well, a signal of QSR is predicted only in the case that the PVED is different from zero, the resonance condition being independent on tunneling between the two enantiomers. It is shown that, at resonance, the fluctuations of the first order contribution to the internal energy are zero. Due to the small value of the PVED, the resonance would occur in the ultracold regime. Some proposals concerning the external driving field are suggested.

1. Introduction

Biological homochirality, that is, the almost exclusive one-handedness of chiral molecules found in living systems (D-sugars and L-aminoacids) is one of the fundamental problems of science which still remains unsolved.[1] In the mid 1950s comes on stage the discovery that parity (P), the symmetry operation which inverts the position of all particles with respect to the origin, is violated in the weak interaction.[2,3] This interaction gives rise to the parity violating energy difference (PVED) between the two enantiomers of a chiral molecule. Given the universality of this PVED, it has been suggested as a possible origin of biological homochirality, although due to its small value, the enantioselection would have taken place through powerful mechanisms of amplification as those involving nonlinear processes in systems far from equilibrium.[4,5] Although the weak interaction has been extensively studied and observed in atoms,[6,7] it has only been predicted in molecules. Electroweak quantum chemistry calculations predict the PVED to be between 10^{-13} and 10^{-21} eV[8–11] but no conclusive energy difference has been reported, for instance, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV.[12] It is however noticeable the experimental results of Wang *et al.*[13,14] in which a chiral discriminating phase transition without conformational changes was obtained at temperature 77–300 K for D/L-alanine and valine. It was interpreted as a manifestation of the PVED and related to the phase transition postulated by Salam.[15] It is also of interest the evidence obtained[16] of the differences in structural transitions between poly-L- and poly-D-amino acids of equal length in *ortho*-H_2O, attributed to an amplification mechanism of the PVED in the α-helix autocatalytic formation. Other kind of experiments have been proposed, based on the pioneering work of Harris and Stodolsky,[17] dealing with the electroweak optical activity of chiral molecules.[18–20] As it is well known, the parity violating signals are easily masked by thermal effects, being highly desirable to reach cold or ultracold regimes in the laboratory.[21,22] In this sense, we have studied in recent works the role of classical and quantum statistics in the thermodynamics of chiral molecules, suggesting some experiments to detect the PVED with classical[20,23] and Bose-condensed[24] gases.

In order to explore physical or chemical phenomena where the tiny PVED would manifest itself, the mechanism of the quantum stochastic resonance (QSR) in chiral molecules is here analyzed. The chiral molecule is described by a two-state system in an asymmetric double well potential coupled to a heat bath and subjected to an external periodic driving field which biases the two minima of the well alternatively. As it is known, spin-boson systems have been active object of study since the works of Leggett and coworkers,[25,26] and their application to P-violating chiral molecules is found in the pioneering works of Harris and Silbey.[27–29] However, as far as we know, the results of a driven spin-boson system has never been applied to the case of P-violating chiral molecules. We restrict our study to very low temperatures where deep quantum tunneling is the only mechanism for barrier crossing. In this regime, QSR has been studied and various novel phenomena predicted.[30–32] Following such previous works, it is shown that for low viscous friction, and in the linear response regime, QSR in the optical activity of the sample is predicted only when there is a non-zero PVED; the condition of resonance being independent of tunneling. We also interpret the resonance conditions in terms of the fluctuations of the internal energy. Finally, the characteristics of the driving field are discussed.

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2. Characterization and interpretation of QSR in chiral molecules

We consider a two-level system in an asymmetric double well potential where the PVED is the static energy difference between the two minima. The system is coupled to a bath of harmonic oscillators by means of a bilinear interaction in the system-bath coordinates. An external harmonic force rises and lowers in an alternate way each one of the two minima of the well. Then, in the localized basis, $|L\rangle$, $|R\rangle$, of the molecule, the driven spin-boson Hamiltonian reads ($\hbar = 1$)[26]

$$H = -\frac{1}{2}\delta\sigma_x - \frac{1}{2}(\varepsilon_{PV} + \varepsilon\cos(\Omega t))\sigma_z + \frac{1}{2}\sum_j \left(\frac{p_j^2}{m_j} + m_j\omega_j^2 x_j^2 - c_j x_j a\sigma_z\right), \quad (1)$$

where $\sigma_{x,z}$ are the Pauli matrices, δ is the tunneling splitting between the eigenstates of the symmetric double well, ε_{PV} is the PVED between L and R enantiomers, $\varepsilon\cos(\Omega t)$ is the interaction energy of the molecule with the periodic external field of frequency Ω, x_j are the coordinates of the bath oscillators of frequency ω_j, a is the distance between the two minima of the double well and c_j are coupling constants. As it is known, the eigenstates $|1\rangle$ (lower), $|2\rangle$ (upper) of the isolated asymmetric molecular system have the energy eigenvalues $E_{1,2}(t) = \mp\Delta(t)$ when an appropriate energy origin is chosen, with $\Delta(t) \equiv [\varepsilon_{PV}^2 + \varepsilon^2(t) + \delta^2]^{1/2}$. For the spectral density of the environment, $J(\omega)$, Ohmic dissipation $J(\omega) = (2\pi/a^2)\alpha\omega e^{-\omega/\omega_c}$ is assumed, where ω_c is a cutoff frequency[25,26] and α is the dimensionless coupling strength quantifying the viscous friction. It will be taken $\alpha = 1/2$ to exploit the full analicity of this case.[31] We focus on the dynamical quantity of interest

$$P(t) \equiv \langle\sigma_z(t)\rangle_{QS} = n_L(t) - n_R(t)$$

where $n_{L,R}$ are the respective population of the molecules in L and R conformations. Such a population difference is proportional to the optical activity of the sample. As usual, $\langle\ldots\rangle_{QS}$ involves quantum statistical average over the bath degrees of freedom. As is known, for times t large compared to the time scale of the transient dynamics, the asymptotic value of $P(t)$ can be expressed as[30]

$$P_{as}(t) = \sum_{m=-\infty}^{\infty} P^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}. \quad (2)$$

The square amplitudes $|P^{(m)}|^2$ are directly related to the intensities of the δ-spikes of the power spectrum. The scaled spectral amplification in the mth frequency is given by η_m which is proportional to the ratio $|P^{(m)}/\varepsilon|^2$. Furthermore, other magnitudes derived from P_{as} also display the same behavior with time as, for instance, the internal energy U_{as} and the specific heat $C_{v,as}$:

$$U_{as}(t) = \sum_{m=-\infty}^{\infty} U^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}, \quad (3)$$

$$C_{v,as}(t) = \sum_{m=-\infty}^{\infty} C_v^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}, \quad (4)$$

where $C_v^{(m)} = \partial U^{(m)}/\partial T$.

In the linear response regime, which is the appropriate regime to study the tiny P-odd effect predicted, only the first two contributions, $m = 0$ and $m = \pm 1$ of $P_{as}(t)$ are important. Following the standard procedure,[26] we have for the zeroth-order (in the absence of driving) contribution,

$$P^{(0)} \equiv \langle\sigma_z\rangle_{QS}^{(0)} = \frac{\varepsilon_{PV}}{\Delta_0}\tanh\beta\frac{\Delta_0}{2}, \quad (5)$$

where $\Delta_0 \equiv \sqrt{\delta^2 + \varepsilon_{PV}^2}$ and $\beta = 1/(k_B T)$ with T the temperature and k_B the Boltzman constant. The non-zero optical activity derived from this result is due to the PVED between enantiomers, ε_{PV}. Eqn (5) gives the population difference in thermal equilibrium without external driving field, that we have already obtained and discussed in a previous work.[23] It was deduced that the internal energy $U^{(0)} = -(\Delta_0/2)\tanh(\beta\Delta_0/2)$, and using eqn (5), it can be reexpressed as

$$U^{(0)} = -\frac{\Delta_0^2}{\varepsilon_{PV}}P^{(0)}. \quad (6)$$

We note at this point that from the specific heat $C_v^{(0)} = \partial U^{(0)}/\partial T$ and the condition $\partial C_v^{(0)}/\partial T = 0$, a critical temperature, T_c, is defined to be[23]

$$\beta_c\frac{\Delta_0}{2}\tanh\beta_c\frac{\Delta_0}{2} = 1, \quad (7)$$

which is interpreted as the temperature which separates the region in which tunneling and parity violation compete with thermal effects.

Now we focus on $P^{(1)}$ which is related, by Kubo's formula,[33] to the linear susceptibility of the system. Following the standard procedure exposed, for example, in Weiss's book,[26] assuming low viscous friction and the restrictions $\Omega\beta \ll 1$, $\varepsilon\beta \ll 1$ and $\varepsilon < \varepsilon_{PV}$, the first-order contribution of the response of our system to the external amplitude ε is expressed as

$$P^{(1)} \equiv \langle\sigma_z\rangle_{QS}^{(1)} = \varepsilon\hat{\chi}(\Omega) = \frac{\varepsilon}{4}\frac{\lambda^2}{\lambda^2+\Omega^2}f(\beta,\varepsilon_{PV}), \quad (8)$$

where

$$f(\beta,\varepsilon_{PV}) = \beta\,\mathrm{sech}^2\beta\frac{\varepsilon_{PV}}{2} \quad (9)$$

and, for Ohmic dissipation and $\alpha = 1/2$, we have $\lambda = \pi\Delta_0^2/(2\omega_c)$.

Thus, from eqn (5), (8) and (9), the asymptotic limit of the population difference $P(t)$, up to first order in the energy of the coupling to the external field, is given by

$$P_{as}(t) = \frac{\varepsilon_{PV}}{\Delta_0}\tanh\beta\frac{\Delta_0}{2} + \frac{\varepsilon}{2}\beta\,\mathrm{sech}^2\left(\beta\frac{\varepsilon_{PV}}{2}\right)\frac{\lambda^2}{\lambda^2+\Omega^2}\cos(\Omega t). \quad (10)$$

provided $\varepsilon,\Omega \ll kT_B$ and $\varepsilon < \varepsilon_{PV}$.

It is easy to see that the spectral amplification, given by η_1, displays a maximum with respect to the temperature, this being the signal of QSR. The temperature at which the

maximum occurs, the quantum stochastic temperature, T_{st}, is obtained from the condition $\partial P^{(1)}/\partial T = 0$, which reads

$$\beta_{st}\varepsilon_{PV}\tanh\beta_{st}\frac{\varepsilon_{PV}}{2} = 1, \tag{11}$$

or

$$k_B T_{st} \approx 0.65\varepsilon_{PV}, \tag{12}$$

which is in quantitative accord with the fact that $k_B T_{st}$ is of the order of the static asymmetry.[30] We note the similarity between eqn (7) and (11), pointing out that the main difference between T_c and T_{st} is that the former depends on δ and ε_{PV}, whereas the latter only depends on ε_{PV}. The existence of ε_{PV}, that is, of the PVED between enantiomers, could then be manifested through the existence of the QSR in the population difference between enantiomers, that is, in the optical activity of the sample, since the maximum of $P^{(1)}$ disappears for $\varepsilon_{PV} = 0$. In Fig. 1, the amplification, $P^{(1)}/\varepsilon$, is plotted as a function of the temperature and ε_{PV}, in a range of ε_{PV} values around 10^{-14} eV, and taking the factor $\lambda^2/(\lambda^2 + \Omega^2)$ as unity. It is seen from Fig. 1 that the maximum increases as ε_{PV} decreases. However, when ε_{PV} increases, the position of the maximum is shifted to higher temperatures but with a smaller amplification. In any case, given the small value predicted for ε_{PV}, the maximum lies in the very deep ultracold regime ($\sim 10^{-10}$ K in the Figure). We remark that the QSR arises only for low viscous friction in the presence of a non-zero ε_{PV}, the condition of the maximum being independent of the tunneling value.

Concerning the internal energy, we now proceed in an analogous way to that followed for the zeroth-order contribution. Thus, the first-order contribution to the internal energy $U^{(1)}$ can be expressed as

$$U^{(1)} = -\frac{\Delta_0^2}{\varepsilon_{PV}}P^{(1)}, \tag{13}$$

resulting into the first-order heat capacity $C_v^{(1)} = \partial U^{(1)}/\partial T$, given by

$$C_v^{(1)} = -\frac{\Delta_0^2}{\varepsilon_{PV}}\frac{\partial P^{(1)}}{\partial T}. \tag{14}$$

Thus, the conditions where there is a maximum in $P^{(1)}$ are equivalent to the conditions where $C_v^{(1)} = 0$. Hence, QSR would occur at a temperature T_{st} at which there are no fluctuations in the first-order internal energy contribution and, therefore, in the population difference $P^{(1)}$. In this situation, $C_v = C_v^{(0)}$ in the linear response regime.

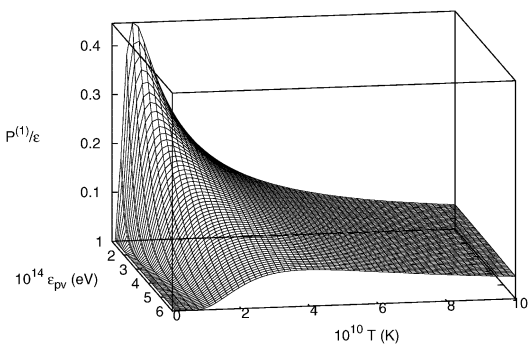

Fig. 1 Amplification $P^{(1)}/\varepsilon$ *versus* temperature T of the order of 10^{-10} K, and *versus* ε_{PV} of the order of 10^{-14} eV is plotted to show the quantum stochastic resonance in chiral molecules (see the text).

Table 1 ε_{PV}, δ, T_c and T_{st} are shown for some selected molecules. The orders of magnitude of ε_{PV} and δ have been taken from the review of Quack[10]

Molecule	ε_{PV}/eV	δ/eV	T_c/K	T_{st}/K
H_2O_2	10^{-18}	10^{-4}	1	10^{-14}
H_2S_2	10^{-16}	10^{-10}	10^{-6}	10^{-12}
H_2Te_2	10^{-13}	10^{-12}	10^{-8}	10^{-9}
CHFBrCl	10^{-16}	Very small	10^{-12}	10^{-12}

Table 1 shows a short list of selected chiral molecules[10] with the orders of magnitude of their corresponding temperatures T_{st} at which QSR would appear together with the critical temperatures T_c defined in eqn (7) associated with $C_v^{(0)}$.

Notice the different orders of magnitude of T_c and T_{st} in the cases where the tunneling splitting is much greater than ε_{PV}. This is due to the fact that T_{st} does not depend on δ whereas T_c does.

We must note that the two-state model here applied is valid only in the case that the energy splitting between the two levels, given by $\sqrt{\delta^2 + \varepsilon_{PV}^2}$, is much smaller than the energy of the first excited rotational level of the molecule, which is of the order of 10^{-3}–10^{-4} eV. Under this condition and for the ultracold regime, the influence of the remaining excited states can be considered negligible. Note that for a high enough δ value this condition can fail.

In order to propose an appropriate external periodic driving field, we must note that, in a non-oriented sample, only a chiral field can induce a different energy in L and R conformations of a chiral molecule. Thus, circular polarized light is a chiral field leading to opposite interaction energy values for the two enantiomers. This energy, averaged for the rapid oscillations of light, has been evaluated,[34] and found to be

$$\varepsilon = \pm\frac{16}{3}EB\omega\frac{R_{n0}}{\omega_{n0}^2 - \omega^2}, \tag{15}$$

where each sign corresponds to each one of the two enantiomers respectively, E and B are the electric and magnetic radiation field, ω_{n0} is the resonance frequency nearest the radiation frequency ω, and R_{n0} is the rotational strength of the optical activity of the molecule, which can be considered to be of the order $R_{n0} \sim 10^{-18}$. If we assume $\omega^2/(\omega_{n0} - \omega^2) \sim 1$, and the frequency of the light $\omega \sim 10^{15}$ rad s^{-1}, we obtain $\varepsilon \sim 10^{-24}E^2$ which, with lasers of about 1 W cm^{-2}, becomes $\varepsilon \sim 10^{-16}$ eV, which is in the appropriate range (lower than ε_{PV}) to study the QSR in chiral molecules. Then, the external driving field could be this type of light, but changing its circular polarization from left to right periodically with low enough frequency Ω. Since $\beta\Omega \ll 1$, and QSR is predicted in the very deep ultracold regime, it is desirable for our system that $\Omega \sim 0.1$ rad s^{-1} or less. It would permit the measurement of optical activity of the sample in a time shorter than $2\pi/\Omega$ and then the detection of the optical activity oscillations, and hence the QSR if $\varepsilon_{PV} \neq 0$. The major problem is, of course, to achieve the ultracold regime.

Another proposal, probably more difficult to implement than the previous one, would consist of an oriented sample where opposite enantiomers have their permanent dipole moments, **d**, oriented in opposite directions. Then, an external electric field **E** is able to produce an interaction energy $\pm\mathbf{E}\cdot\mathbf{d}$ of opposite sign for each enantiomer. The electric field must then oscillate periodically with frequency Ω, and the value of E must be extremely small to get an ε value smaller than ε_{PV}. The requirements for Ω and the temperature are the same as in the preceding case.

3. Conclusion

This study could be considered as a contribution to the search for the PVED in chiral molecules, of interest in some biochemical models of evolution towards the biological homochirality. For this goal, a QSR analysis has been carried out. Quantum stochastic resonance in the population difference between the two enantiomers of a chiral molecule (and then in the optical activity of the sample) has been studied for P-violating chiral molecules, in the linear response to an external driving periodic field, in the deep quantum regime and under low viscous friction. As was expected, only in the case that a parity violating energy difference between enantiomers exists, a signal of QSR is predicted in the ultracold regime. Thus, any confirmation of the existence of this signal should be an unequivocal signature for parity violation in chiral molecules. The temperature at which QSR is predicted depends only on the static asymmetry, determined by the PVED, being independent on tunneling. In resonance, not only the fluctuations of the first-order population difference are zero, but also those of the first-order contribution to the internal energy. Some proposals are made on the external driving field. It must be chiral if we deal with a non-oriented sample, for example, a light changing its circular polarization from left to right periodically with a change frequency Ω. A small value of Ω would permit optical activity measurements during the oscillations.

Concerning the major problem which is to reach the ultracold regime, we note that it has been reached within the actual experimental capabilities only for diatomic molecules and smaller systems. However, recent works[35] show that it might be possible in the near future to cool polyatomic molecules to ultralow temperatures as well.

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